

XANES and EXAFS Studies for Reduced Cobalt Porphyrins and Phthalocyanines

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Beamline(s): X18B, X19A

Introduction: Others and we have shown that cobalt porphyrins and phthalocyanines are effective photocatalysts in the reduction of CO_2 to CO and formate (D. Behar et al, 1998 and J. Grodkowski et al, 2000). Studies of the mechanism of CO_2 activation in this multi-electron process are currently underway. The site of reduction, metal versus macrocycle, along with changes in the catalysts structural and electronic properties are important in understanding the active species in these catalytic reactions. We undertook XANES and EXAFS studies of chemically reduced Co(II) porphyrin and Co(II) phthalocyanine to further characterize the intermediates generated in the photocatalytic process.

Methods and Materials: Cobalt K-edge XANES and EXAFS measurements were performed at the NSLS beamlines X-18B and X-19A. The samples were prepared using published procedures (L. R. Furenlid et al 1995) and the purity was monitored optically before and after X-ray exposure. X ray absorption spectra were collected in fluorescence mode with a multi-element solid-state detector.

Results: The XANES spectra for a series of cobalt porphyrins in various oxidation and ligation states are shown in Figure 1. The edge positions for Co(III) porphyrins are sensitive to the axial ligands present. The -1 eV edge shift for the chloride versus pyridine complex represents a partial reduction of the Co(III) oxidation state by the chloride ion. The most striking feature of the XANES spectra for Co(II), Co(I) and Co(0) porphyrins is the lack of an edge shift upon reduction, even though they are metal-centered reductions. Similar results were also obtained for the reduction products of Co(II) phthalocyanines which consist of both metal and macrocycle reductions. One explanation for no edge shift upon metal reduction is charge transfer between sodium cations in solution and the cobalt center. This has been ruled out by sequestering the sodium cations using a crown ether, the resulting XANES spectra are unchanged for the reduced Co(II) species.

Conclusions: The metal edge position is sensitive not only to the oxidation state of the metal, but also the ligands. Chloride ion donates more electron density to the cobalt metal than pyridine resulting in a -1 eV shift in the edge position. The lack of an edge shift upon reduction of Co(II) porphyrins and phthalocyanines suggests redistribution of the electron density around the metal onto the ligand π system, thus making the ligands susceptible to hydrogenation which is observed during the photochemical CO_2 .

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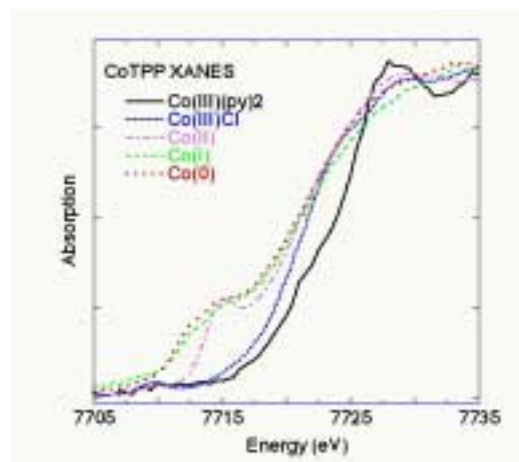


Figure 1. XANES spectra of cobalt porphyrins.